Critical Review

Ligand Design for Functional Metal-Organic Frameworks

Filipe A. Almeida Paz,*[a] **Jacek Klinowski**,*[b]
Sérgio M. F. Vilela,[a,c] **João P. C. Tomé**[c]
José A. S. Cavaleiro[c] *and* **João Rocha**[a]

A contribution from

[a] Department of Chemistry, CICECO, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

[b] Department of Chemistry, University of Cambridge, Lensfield Road, CB2 1EW Cambridge, U.K.

[c] Department of Chemistry, QOPNA, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

Contacts:
E-mail filipe.paz@ua.pt
Telephone: +351 234370200, Extension 23553
Fax: +351 234370084

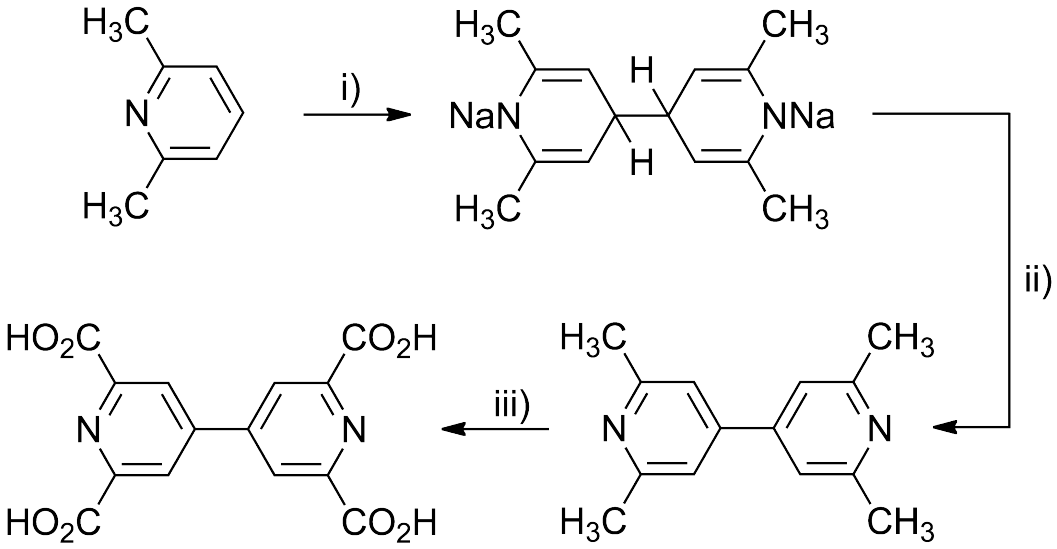
E-mail: jk18@hermes.cam.ac.uk
Telephone: +44 1223 336514
Fax: +44 1223 336362

Electronic Supporting Information

Table of Contents

1 - Synthetic Procedures

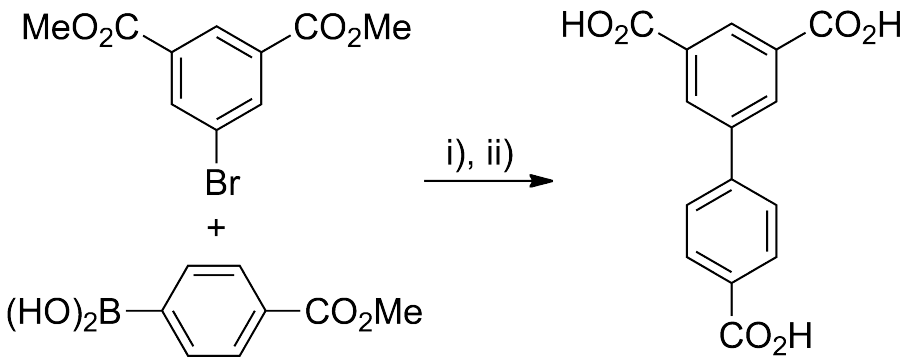
1.1 - 4,4'-Bipyridine-2,2',6,6'-tetracarboxylic acid



i) Na, THF, r.t., N_2, 2-24 h (Caution: reaction under dry tetrahydrofuran!); ii) SO_2, 4-6 h; iii) H_2SO_4, CrO_3, 75 ºC, 2 h (Caution: care about chromium(VI) species as they are carcinogenic!).

Figure S1 - Synthesis of 4,4'-bipyridine-2,2',6,6'-tetracarboxylic acid according to Lin *et al.*[1]

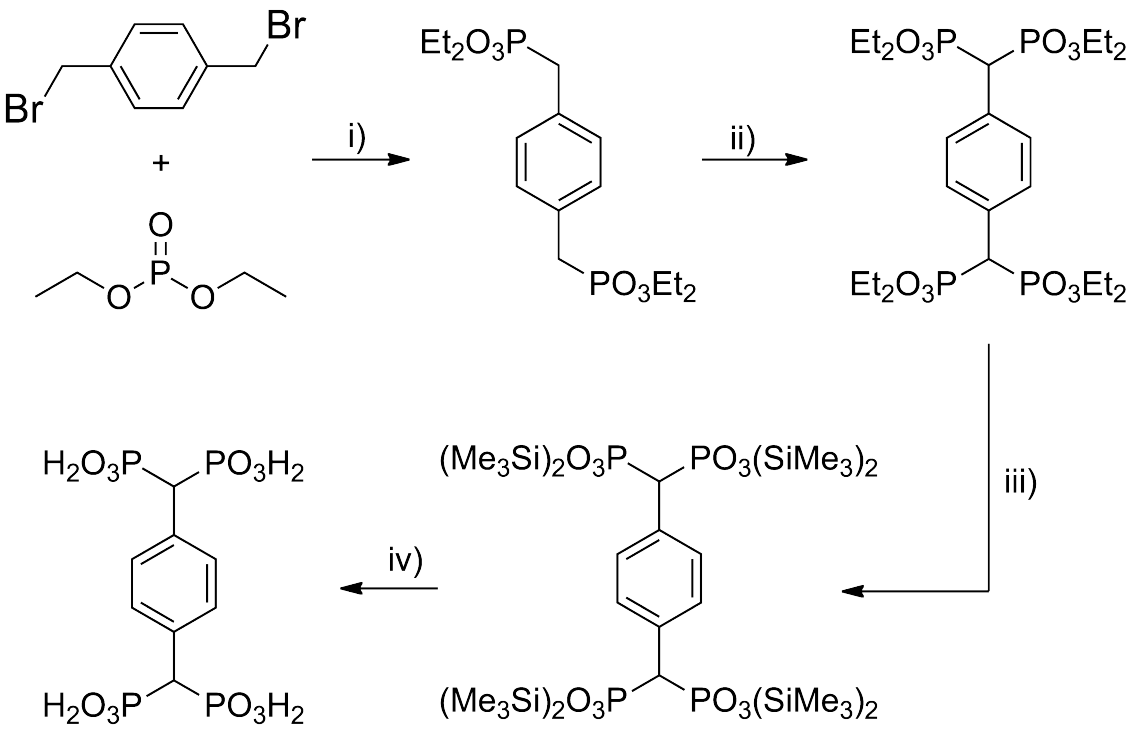
1.2 - Biphenyl-3,4',5-tricarboxylic acid



i) a) Toluene, EtOH, K_2CO_3, H_2O; b) $Pd(PPh_3)_4$, reflux, N_2, overnight; ii) a) dioxane, KOH, reflux, 12 h; b) HCl.

Figure S2 - Synthesis of biphenyl-3,4',5-tricarboxylic acid according to Wong-Foy *et al.*[2]

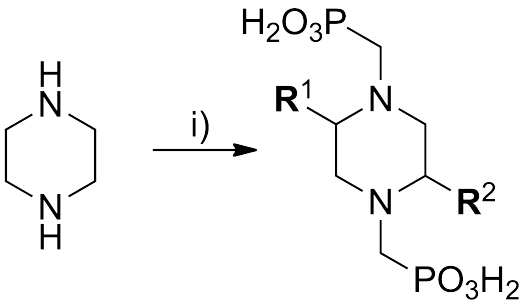
1.3 - [1,4-Phenylenebis(methanetriyl)]tetraphosphonic acid



i) Dry toluene, 110 ºC, 20 h; ii) a) LDA, THF, -78 ºC (Caution: lithium diisopropylamide is highly toxic by inhalation!); b) $ClPO_3Et_2$, r.t.; c) NH_4Cl, 2h; iii) CH_2Cl_2, Me_3SiBr, r.t.; iv) MeOH.

Figure S3 - Synthesis of [1,4-phenylenebis(methanetriyl)]tetra-phosphonic acid according to Plabst and Bein.[3]

1.4 - *N,N'*-Piperazinebis(methylenephosphonic acid)
2-Methyl-*N,N'*-piperazinebis(methylenephosphonic acid)
2,5-Dimethyl-*N,N'*-piperazinebis(methylenephosphonic acid)

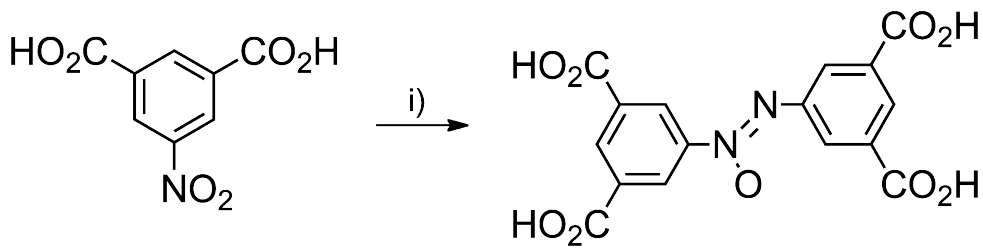


R^1 = H or CH_3
R^2 = H or CH_3

i) H_3PO_3, HBr, H_2O, CH_2O, reflux, 20 h.

Figure S4- - Synthesis of (R^1 = H and R^2 = H) *N,N'*-piperazinebis-(methylenephosphonic acid), according to Groves *et al.*,[4] and of (R^1 = CH_3 and R^2 = H) 2-methyl-*N,N'*-piperazinebis(methylenephosphonic acid) and (R^1 = CH_3 and R^2 = CH_3) 2,5-dimethyl-*N,N'*-piperazinebis(methylene-phosphonic acid) according to Mowat *et al.*[5]

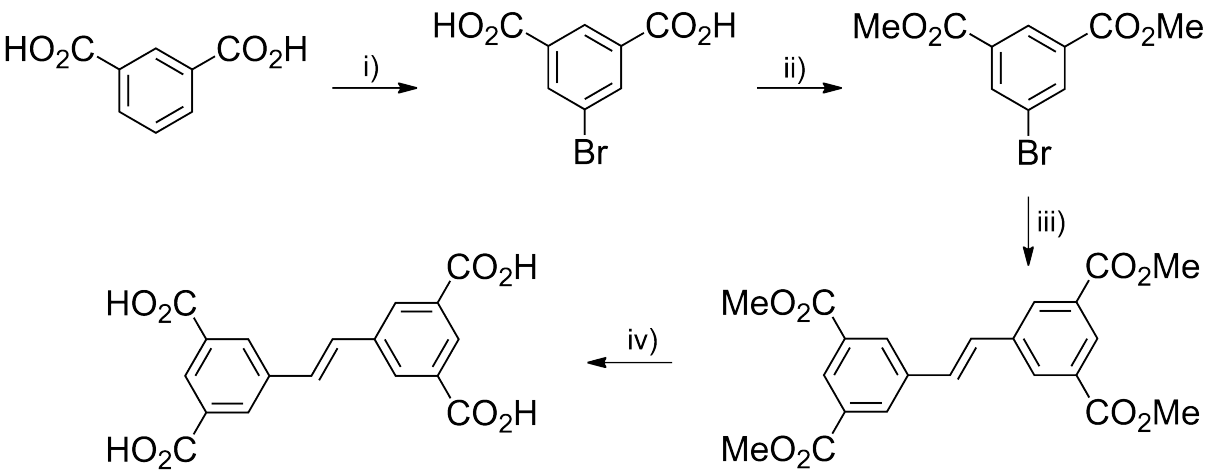
1.5 - Azoxybenzene-3,3′,5,5′-tetracarboxylic acid



i) Zn, NaOH, EtOH, H_2O, reflux, 12h.

Figure S5 - Synthesis of azoxybenzene-3,3′,5,5′-tetracarboxylic acid according to Wang *et al.*[6]

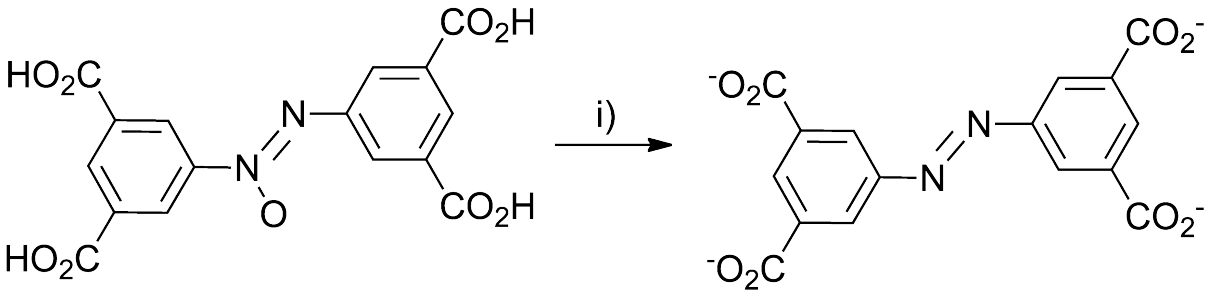
1.6 - *trans*-Stilbene-3,3′,5,5′-tetracarboxylic acid



i) Br_2, H_2SO_4 (Caution: bromine is highly toxic by inhalation!); ii) MeOH, H_2SO_4; iii) $Pd(OAc)_2$ (1 mol%), Pd(*o*-Tolyl)$_3$ (1 mol%), NMP, Et_3N, ethene (1.5 bar), 100 ºC, 25.5 h; iv) a) NaOH, THF, MeOH; b) HCl.

Figure S6 - Synthesis of *trans*-stilbene-3,3′,5,5′-tetracarboxylic acid according to Wang *et al.*[6]

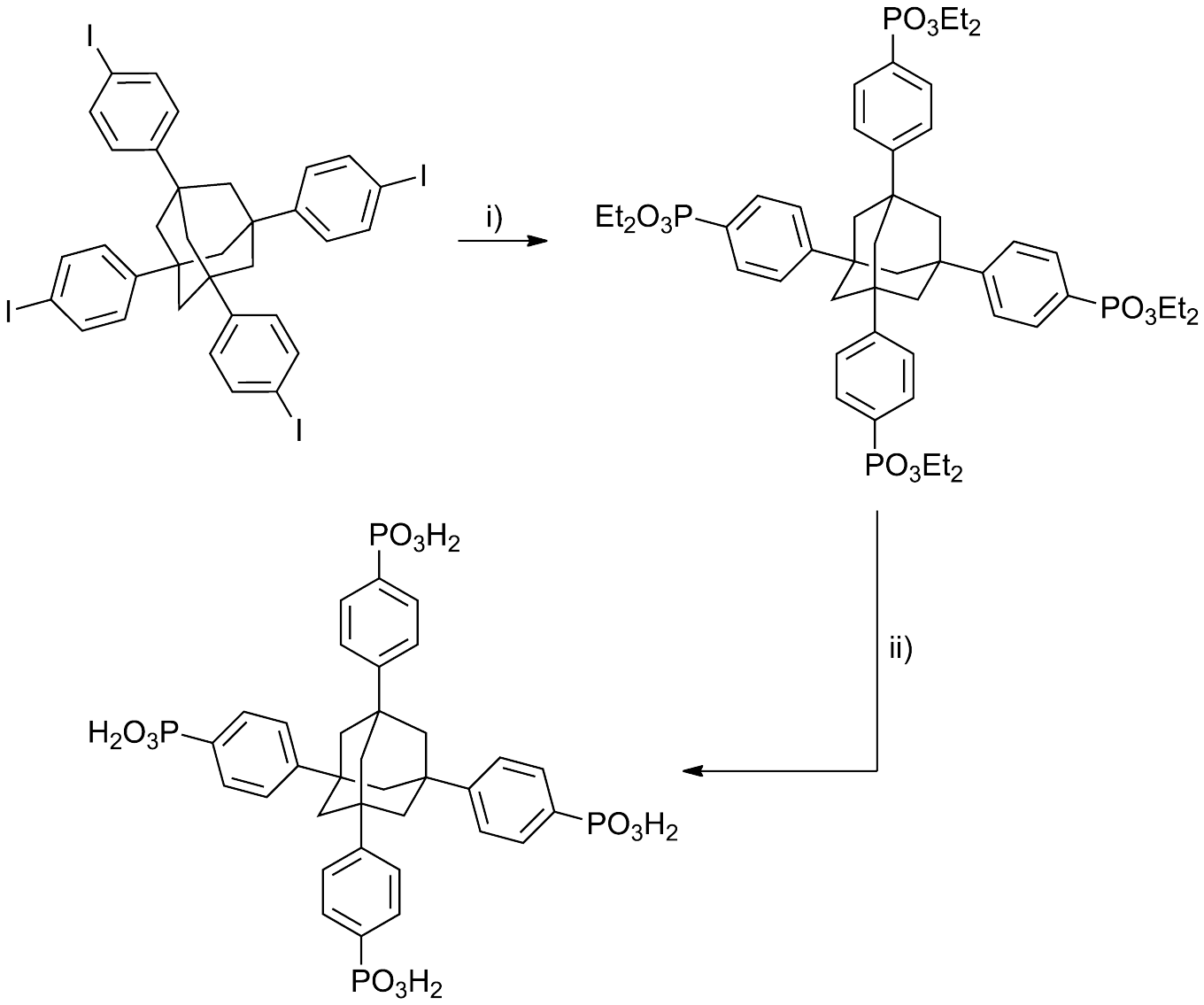
1.7 - Azobenzene-3,3′,5,5′-tetracarboxylate



i) Reduction under solvothermal conditions.

Figure S7 - Synthesis of azobenzene-3,3′,5,5′-tetracarboxylate according to Wang *et al.*[6]

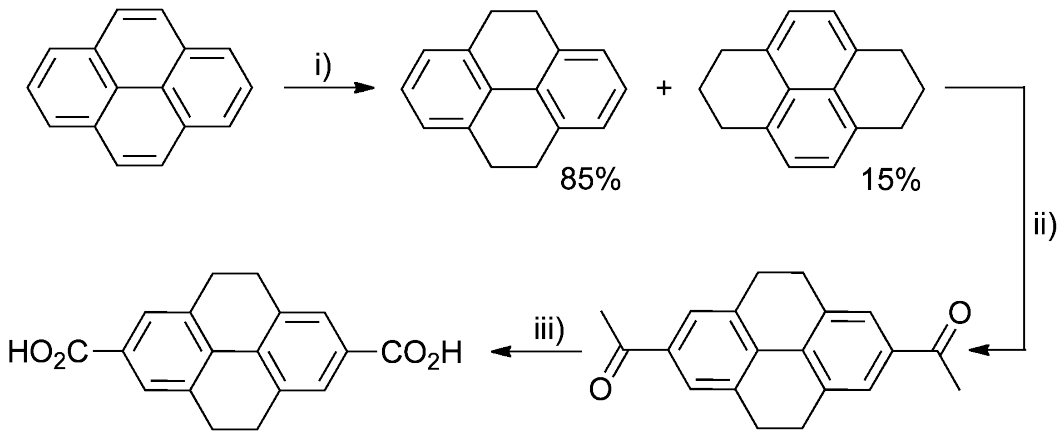
1.8 - 1,3,5,7-Tetrakis(4-phosphonophenyl)adamantane



i) $PdCl_2(PPh_3)$, $HPO(OEt)_2$, Et_3N, benzene, 80 ºC, 72 h; ii) HCl, reflux, 24 h.

Figure S8 - Synthesis of 1,3,5,7-tetrakis(4-phosphonophenyl)adamantane according to Vasylyev *et al.*[7]

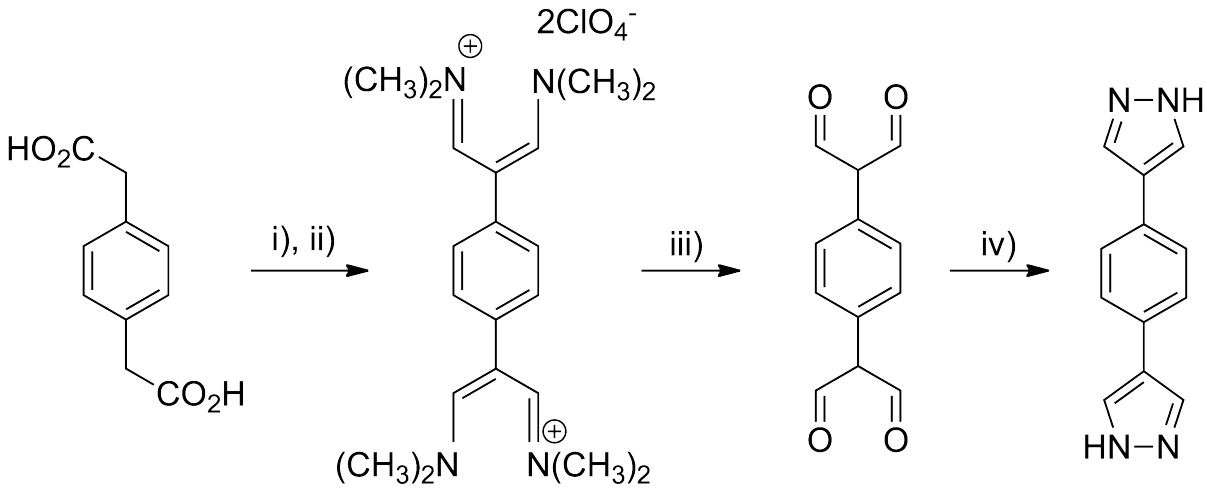
1.9 - 4,5,9,10-Tetrahydropyrene-2,7-dicarboxylic acid



i) a) Raney nickel, EtOAc, 2 d (Caution: do not let the Raney nickel became dry!); b) H_2 (45 psi.), 10% Pd/C, EtOAc, 3 d; ii) AcCl, $AlCl_3$, CH_2Cl_2, N_2, 0 ºC to r.t., 2.5 h (Caution: $AlCl_3$ releases HCl fumes!); iii) Br_2, NaOH, dioxane/water (Caution: bromine is highly toxic by inhalation!).

Figure S9 - Synthesis of 4,5,9,10-tetrahydropyrene-2,7-dicarboxylic acid according to Connor *et al.*[8]

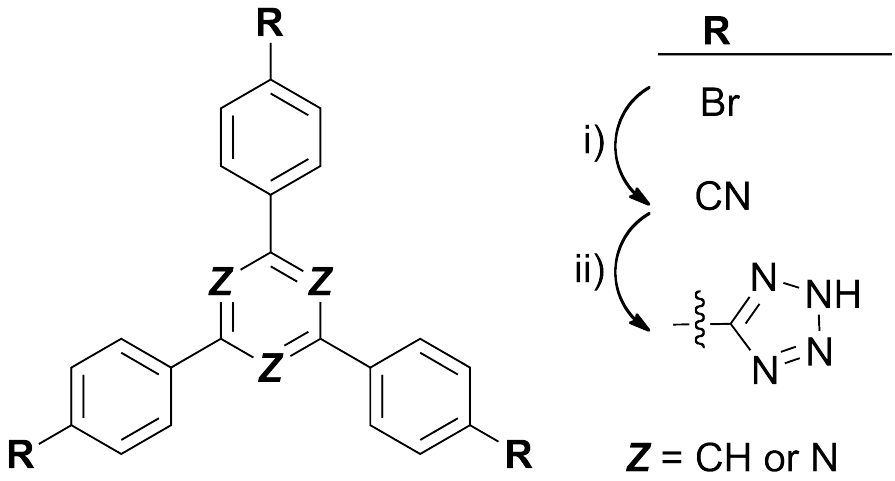
1.10 - 1,4-di(1*H*-Pyrazol-4-yl)benzene



i) DMF, $POCl_3$, 90-95 ºC, 4 h (Caution: phosphoryl chloride can release HCl fumes!); ii) $NaClO_4$; iii) a) NaOH, 90 ºC, 7-8 min; b) HCl; iv) N_2H_4, r.t., 15-20 min.

Figure S10 - Synthesis of 1,4-di(1*H*-pyrazol-4-yl)benzene according to Lozan *et al.*[9]

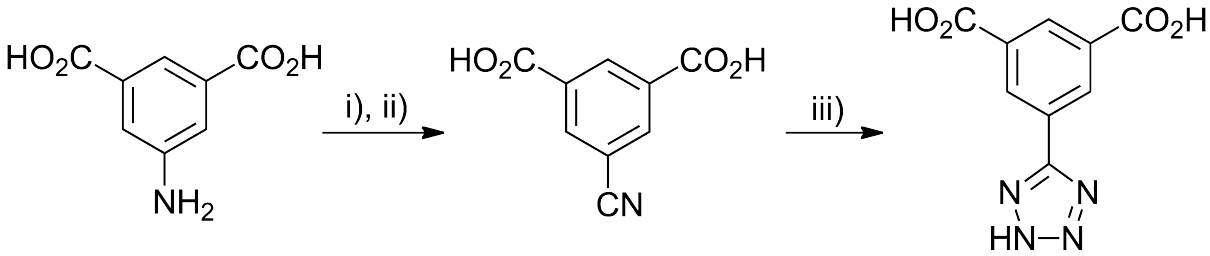
1.11 - 1,3,5-tris[4-(2*H*-Tetrazol-5-yl)phenyl]benzene 2,4,6-tris[4-(2*H*-Tetrazol-5-yl)phenyl]-1,3,5-triazine



i) CuCN, DMF, reflux, N_2, 24 h (Caution: do not let reactions with cyanide salts become acid. HCN is highly toxic by inhalation!); ii) a) NaN_3, $Et_3N \cdot HCl$, toluene, MeOH, reflux, 4 d; b) NaOH, r.t., 30 min (Caution: metal azides and tetrazoles are potentially explosive and should be handled with great care!).

Figure S11 - Synthesis of (*Z* = CH) 1,3,5-tris[4-(2*H*-tetrazol-5-yl)phenyl]benzene and (*Z* = N) 2,4,6-tris[4-(2*H*-tetrazol-5-yl)phenyl]-1,3,5-triazine according to Dincă *et al.*[10]

1.12 - 5-(1*H*-Tetrazol-5-yl)isophthalic acid



i) HCl, $NaNO_2$, 0 °C; ii) NaCN, CuCN, reflux, 40 min (Caution: do not let reactions with cyanide salts become acid. HCN is highly toxic by inhalation!); iii) NaN_3, $ZnBr_2$, H_2O, reflux, 24 h (Caution: metal azides and tetrazoles are explosive and should be handled with great care!).

Figure S12 - Synthesis of 5-(1*H*-tetrazol-5-yl)isophthalic acid according to Demko *et al.*[11] and Ritzen *et al.*[12]

1.13 - 1,3,5-tris[(1,3-Dicarboxylic acid-5-(4-(ethynyl)phenyl))ethynyl]benzene

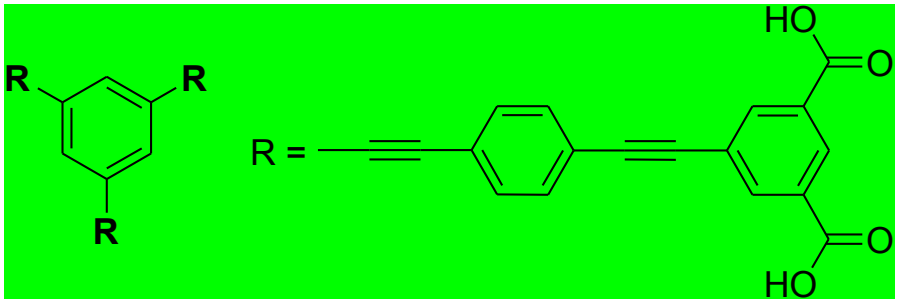
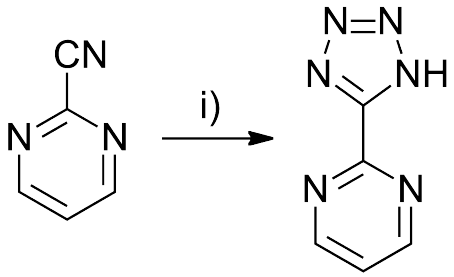


Figure S13 - For a detailed synthetic procedure of 1,3,5-tris[(1,3-dicarboxylic acid-5-(4-(ethynyl)phenyl))ethynyl]benzene see the Electronic Supporting Information of the paper by Farha *et al.*[13]

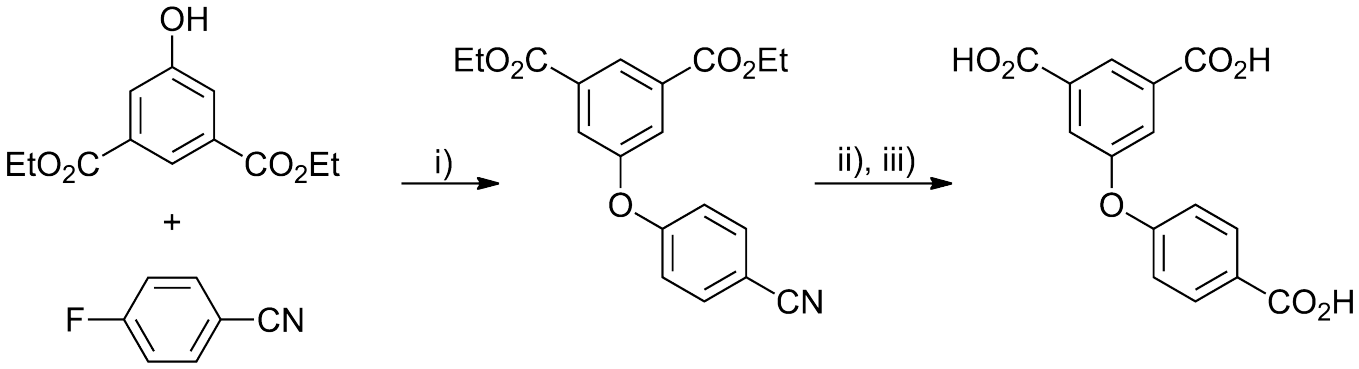
1.14 - 2-(1*H*-Tetrazol-5-yl)pyrimidine



i) NaN_3, MeOH, r.t. (Caution: metal azides and tetrazoles are potentially explosive and should be handled with great care!).

Figure S14 - Synthesis of 2-(1*H*-tetrazol-5-yl)pyrimidine according to Pachfule *et al.*[14]

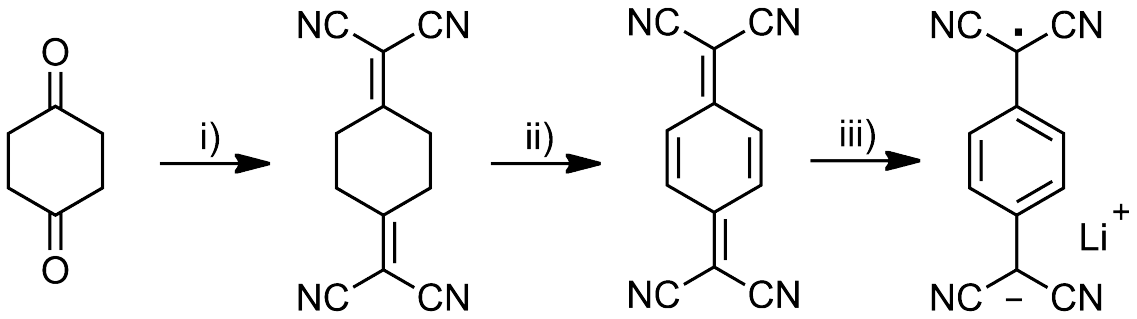
1.15 - 5-(4-Carboxyphenoxy)isophthalic acid



i) K_2CO_3, DMF, 80 ºC, 24 h; ii) NaOH, reflux: iii) HCl.

Figure S15 - Synthesis of 5-(4-carboxyphenoxy)isophthalic acid according to Lama *et al.*[15]

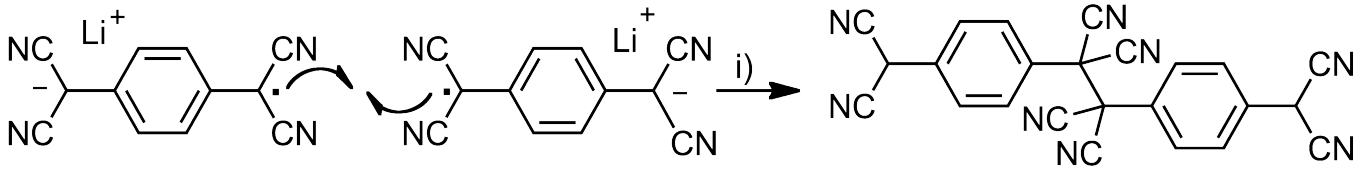
1.16 - Lithium 7,7',8,8'-tetracyanoquinodimethanide(1-)



i) $CNCH_2CN$, CH_3COOH, CH_3COONH_4, reflux, 2 h; ii) Br_2, CH_3CN, C_5H_5N, 20 ºC, N_2, 1 h (Caution: bromine is highly toxic by inhalation!); iii) LiI, CH_3CN.

Figure S16 - Synthesis of lithium 7,7',8,8'-tetracyanoquinodi-methanide(1-) according to Acker and Hertler[16] and Cornelissen *et al.*[17]

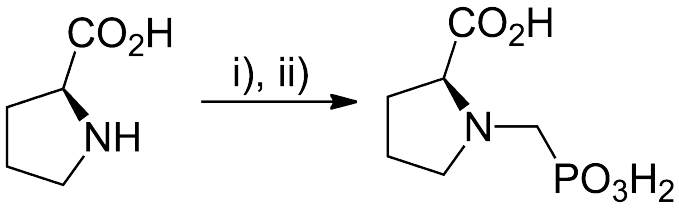
1.17 - 1,2-bis[4-(Dicyanomethyl)phenyl]ethane-1,1,2,2-tetracarbonitrile



i) TCNQ dimer was derived *in situ*, under solvothermal conditions, from σ dimerization of two $TCNQ^-$ anions.

Figure S17 - Synthesis of 1,2-bis[4-(dicyanomethyl)phenyl]ethane-1,1,2,2-tetracarbonitrile according to Shimomura *et al.*[18]

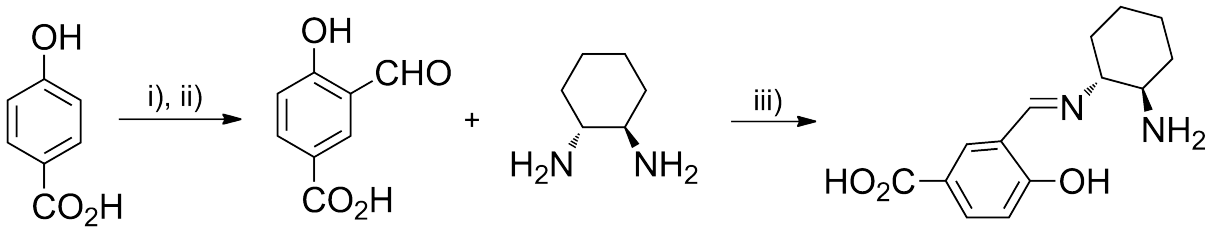
1.18 - (*S*)-*N*-(Phosphonomethyl)proline



i) H_3PO_3, HCl, CH_2O, reflux, 90 min; ii) ethanol, reflux.

Figure S18 - Synthetsis of (*S*)-*N*-(phosphonomethyl)proline according to Yue *et al.*[19]

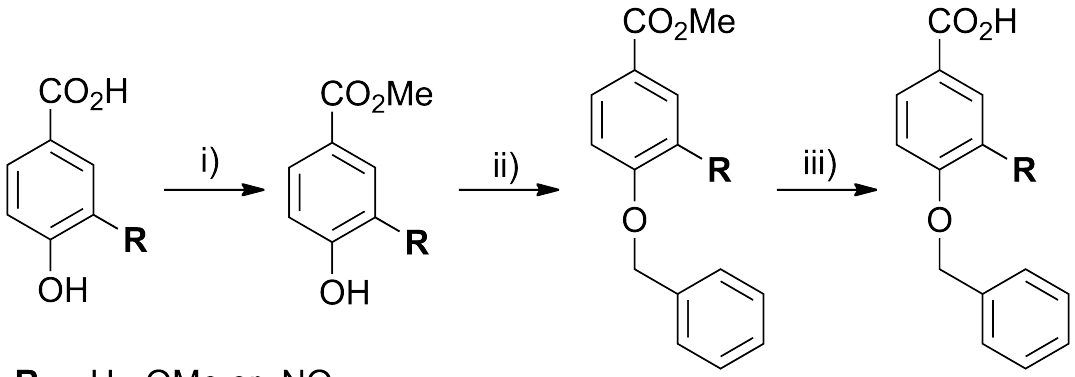
1.19 - 3-[(*E*)-{[(1*R*,2*R*)-2-Aminocyclohexyl]imino}methyl]-4-hydroxybenzoic acid



i) $CHCl_3$, NaOH; ii) HCl; iii) MeOH, reflux, 1 h.

Figure S19 - Synthesis of 3-[(*E*)-{[(1*R*,2*R*)-2-aminocyclohexyl]imino}methyl]-4-hydroxybenzoic acid according to Yuan *et al.*[20]

1.20 - 4-Benzyloxybenzoic acid
4-Benzyloxy-3-methoxybenzoic acid
4-Benzyloxy-3-nitrobenzoic acid

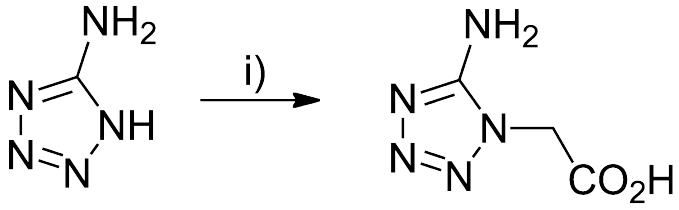


R = -H, -OMe or -NO_2

i) H_2SO_4, MeOH, 24h, 68 ºC; ii) K_2CO_3, C_6H_5-CH_2Br, DMF, 48h, 78 ºC; iii) KOH, EtOH, 24h, 68 ºC.

Figure S20 - Synthesis of (R = H) 4-benzyloxybenzoic, (R = OCH_3) 4-benzyloxy-3-methoxybenzoic and (R = NO_2) 4-benzyloxy-3-nitrobenzoic acids according to Sivakumar *et al.*[21]

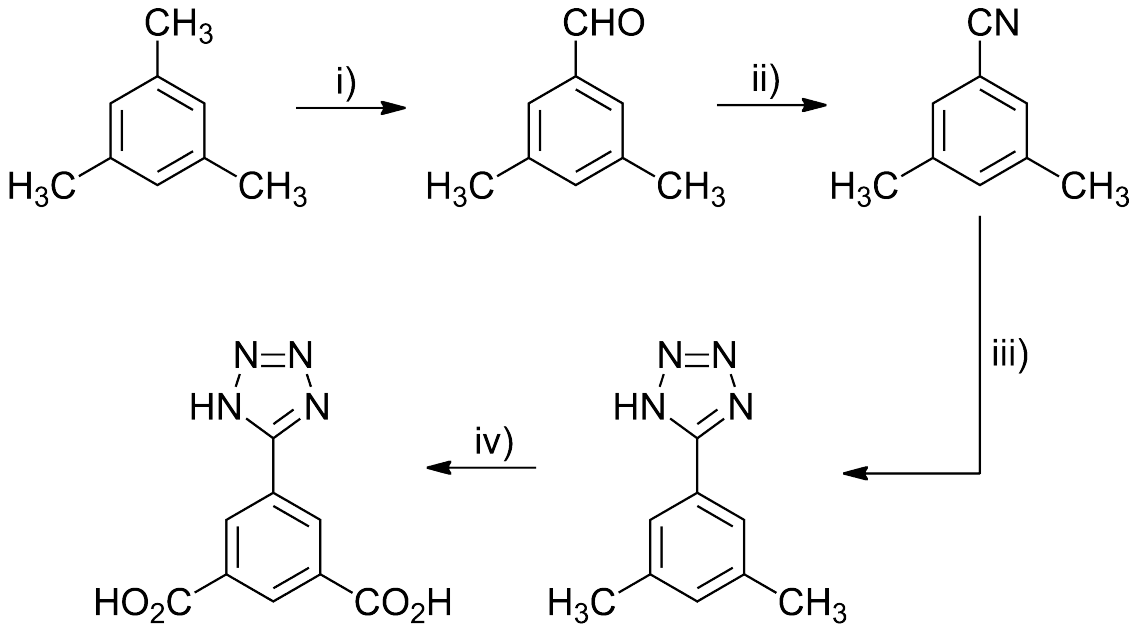
1.21 - (5-Amino-1*H*-tetrazol-1-yl)acetic acid



i) $ClCH_2COOH$, KOH, CH_3OH, reflux, 18-24 h (Caution: tetrazoles are potentially explosive and should be handled with great care!).

Figure S21 - Synthesis of (5-amino-1*H*-tetrazol-1-yl)acetic acid according to Einberg[22] and Li *et al.*[23]

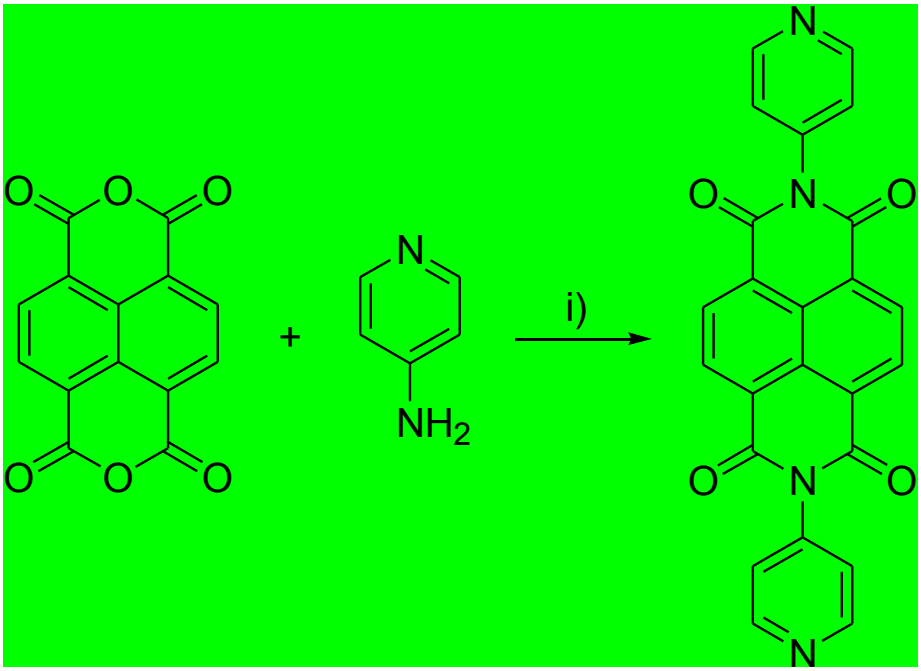
1.22 - 5-(1*H*-Tetrazol-5-yl)isophtalic acid (2nd route)



i) $Ce(NH_4)_2(NO_3)_6$, CH_3COOH; ii) THF, NH_4OH, I_2; iii) NaN_3, NH_4Cl, DMF (Caution: metal azides and tetrazoles are potentially explosive and should be handled with great care!).; iv) $KMnO_4$.

Figure S22 - A different synthesis of 5-(1*H*-tetrazol-5-yl)isophtalic acid according to Qu *et al.*[24]

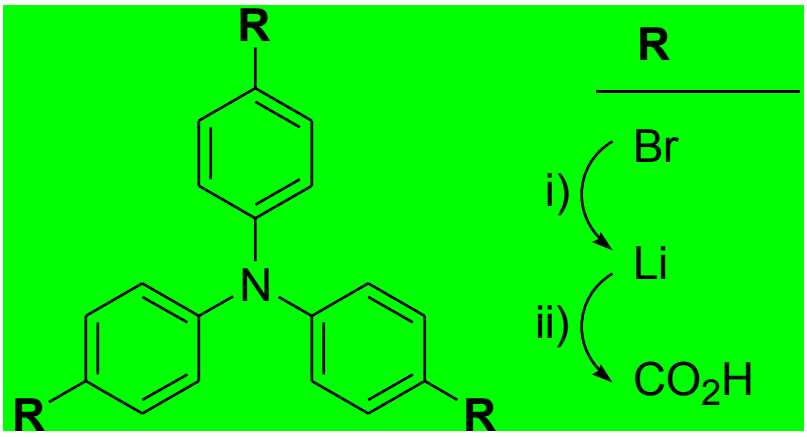
1.23 - *N,N'*-Di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide



i) a) Dry DMF, N_2, reflux, overnight; b) H_2O

Figure S23 - Synthesis of *N,N'*-Di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxy-diimide according to Dinolfo *et al.*[25]

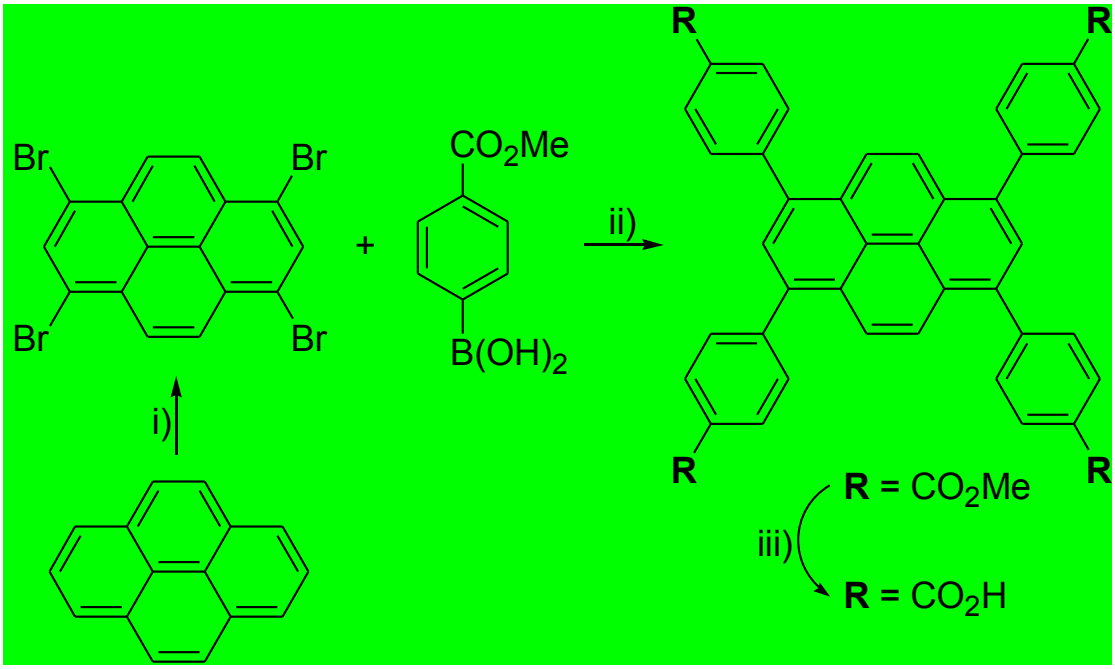
1.24 - 4,4',4''-Nitrilotrisbenzoic acid



i) Et_2O, Ar, *n*-BuLi, r.t. to reflux, 2 h; ii) a) CO_2, 0 °C to r.t., 1 h; b) HCl.

Figure S24 - Synthesis of 4,4',4''-nitrilotrisbenzoic acid according to Dapperheld *et al.*[26]

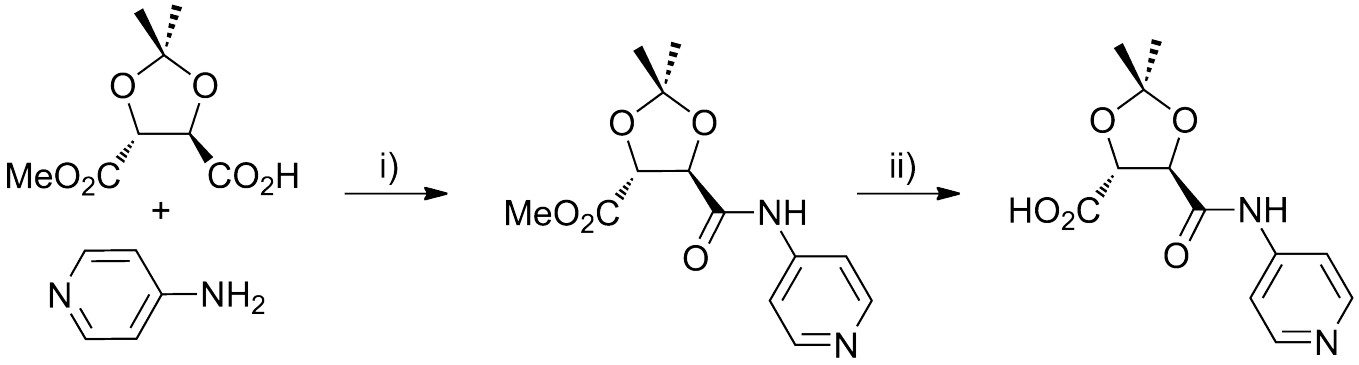
1.25 - 4,4',4'',4'''-(Pyrene-1,3,6,8-tetrayl)tetrabenzoic acid



i) Nitrobenzene, Br_2, 120 ºC, 14 h (Caution: nitrobenzene and bromine are highly toxics by inhalation!); ii) a) $Pd(PPh_3)_4$, K_2CO_3, dry dioxane, N_2, 85 ºC, 72 h; b) H2O/HCl (3:1); iii) a) NaOH, THF/dioxane/H_2O (5:2:2), 85 ºC, overnight; b) H_2O, HCl.

Figure S25 - Synthesis of 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid according to Stylianou *et al.*[27]

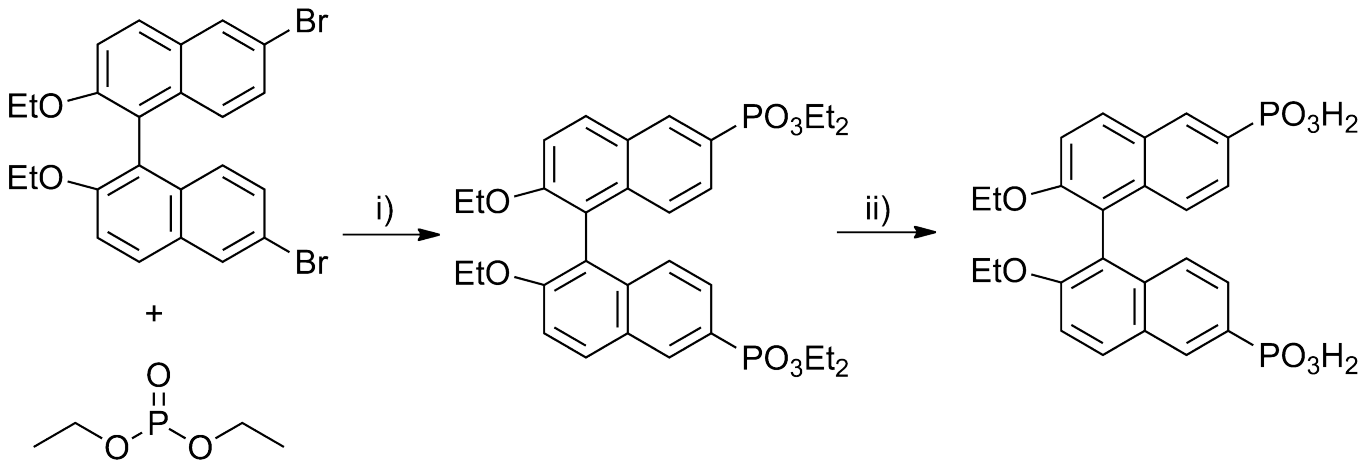
1.26 - (4*R*,5*R*)-2,2-Dimethyl-5-[(pyridin-4-ylamino)carbonyl]-1,3-dioxolane-4-carboxylic acid



i) DCC, CH_2Cl_2, r.t., 5 h; ii) KOH, MeOH, reflux, 8 h.

Figure S26 - Synthesis of (4*R*,5*R*)-2,2-dimethyl-5-[(pyridin-4-ylamino)carbonyl]-1,3-dioxolane-4-carboxylic acid according to Seo *et al.*[28] (for the final product), and Musich and Rapoport[29] (for the starting chemical).

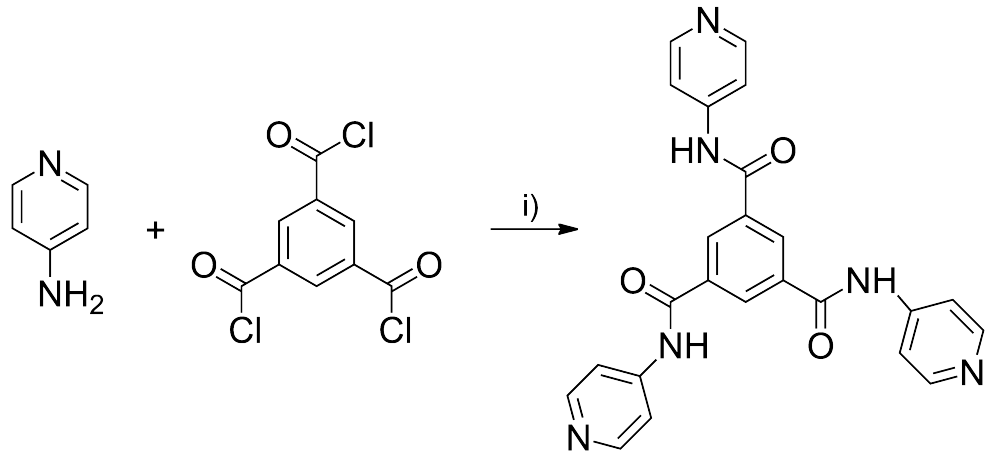
1.27 - 2,2'-Diethoxy-1,1'-binaphthalene-6,6'-diphosphonic acid



i) $Pd(PPh_3)_4$, dry toluene, Et_3N, reflux, N_2, 48 h; ii) a) Me_3SiBr, CH_2Cl_2, r.t, N_2, 24 h; b) MeOH.

Figure S27 - Synthesis of 2,2'-diethoxy-1,1'-binaphthalene-6,6'-diphosphonic acid according to Evans *et al.*[30, 31]

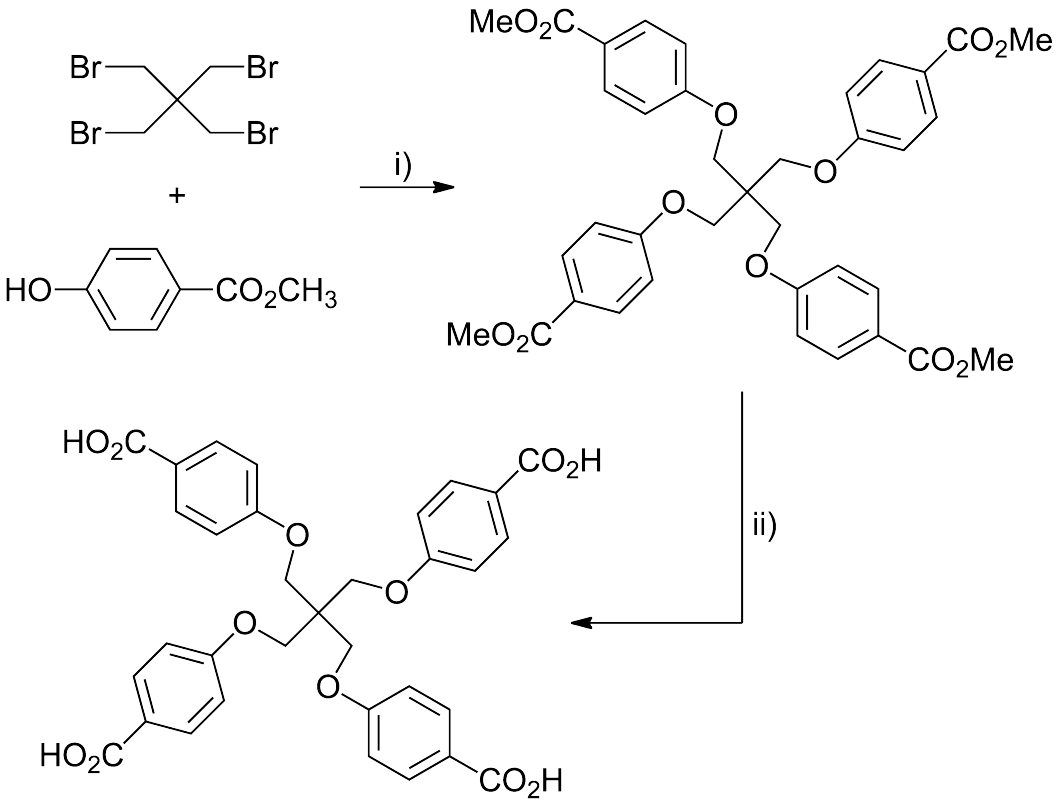
1.28 - N^1,N^3,N^5-tri(Pyridin-4-yl)benzene-1,3,5-tricarboxamide



i) Et_3N, THF, r.t, 7 h (Caution: aniline should be handled carefully!).

Figure S28 - Synthesis of N^1,N^3,N^5-tri(pyridin-4-yl)benzene-1,3,5-tricarboxamide according to Hasegawa *et al.*[32]

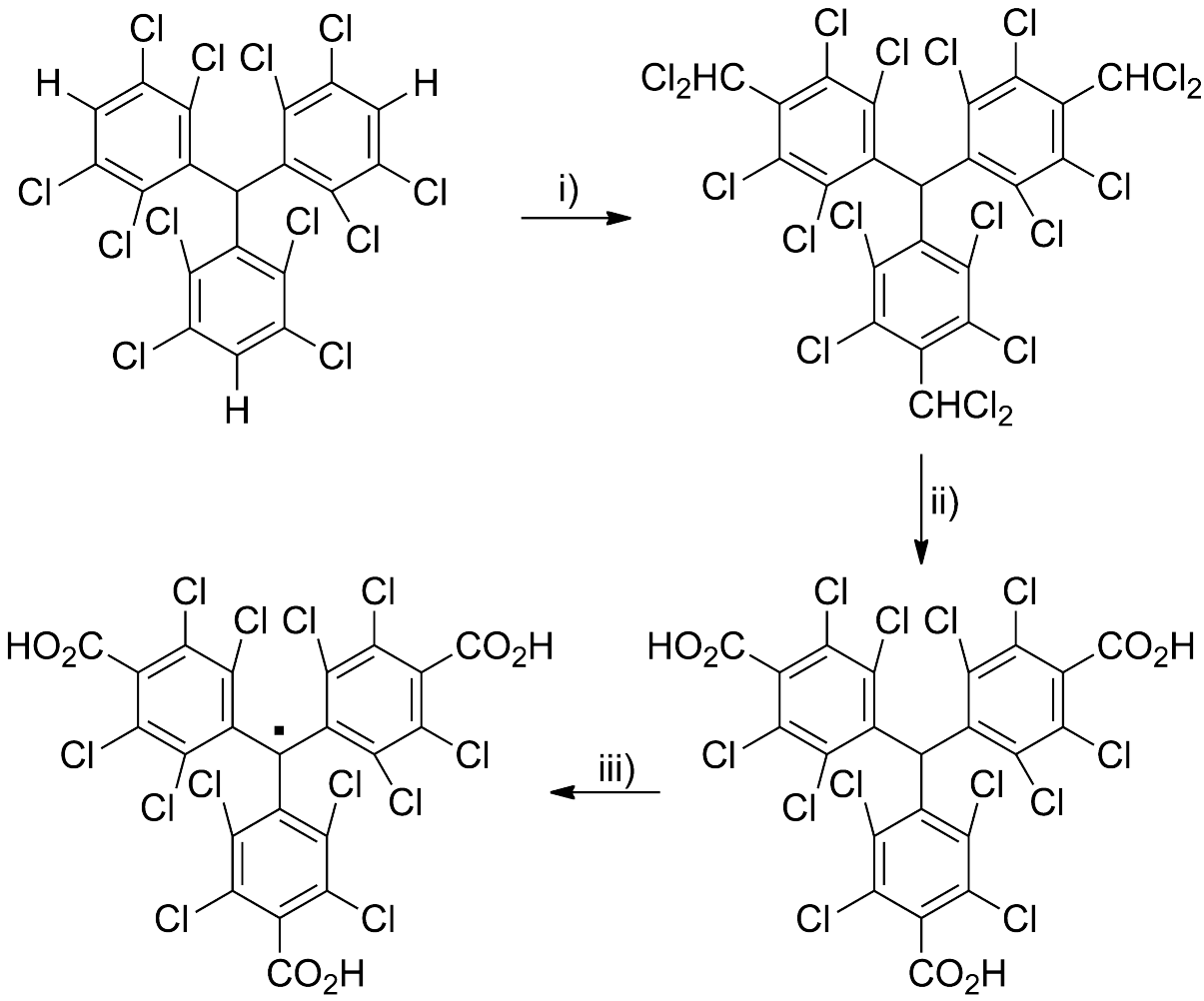
1.29 - Tetrakis[4-(carboxyphenyl)oxymethyl]methane



i) K_2CO_3, DMF, 90 ºC, 92 h; ii) KOH, EtOH, THF, reflux, 2 h.

Figure S29 - Synthesis of tetrakis[4-(carboxyphenyl)oxymethyl]-methane according to Tu *et al.*[33]

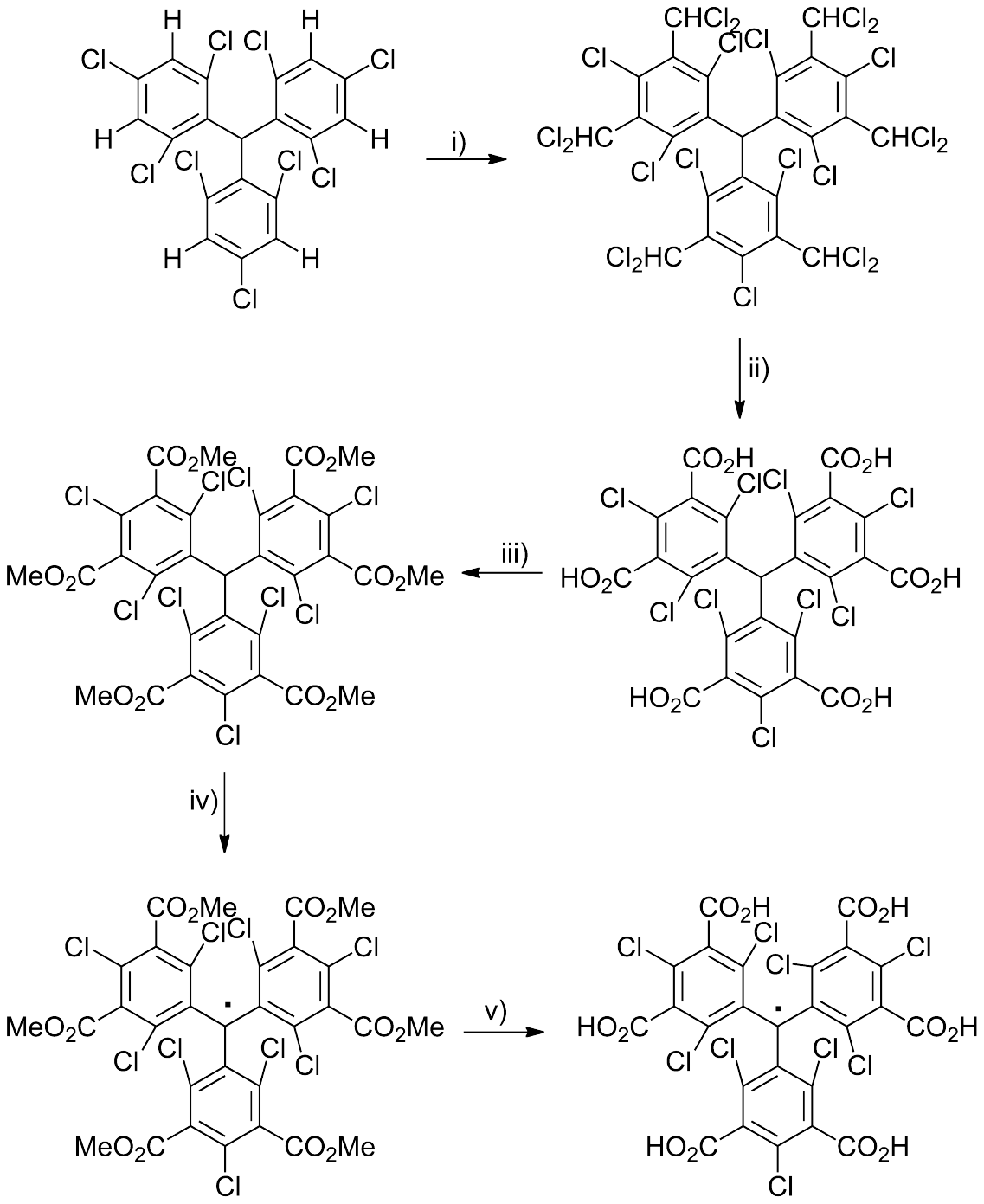
1.30 - tris(2,3,5,6-Tetrachloro-4-carboxy)methyl radical



i) $CHCl_3$, $AlCl_3$ (Caution: aluminum chloride reacts vigorously with water and releases HCl fumes. Dry conditions are required!); ii) fuming sulfuric acid (Caution: H_2SO_4 is highly corrosive!); iii) NaOH, I_2, HCl.

Figure S30 - Synthesis of tris(2,3,5,6-tetrachloro-4-carboxy)methyl radical according to Maspoch *et al.*[34]

1.31 - tris(2,4,6-Trichloro-3,5-dicarboxy)methyl radical

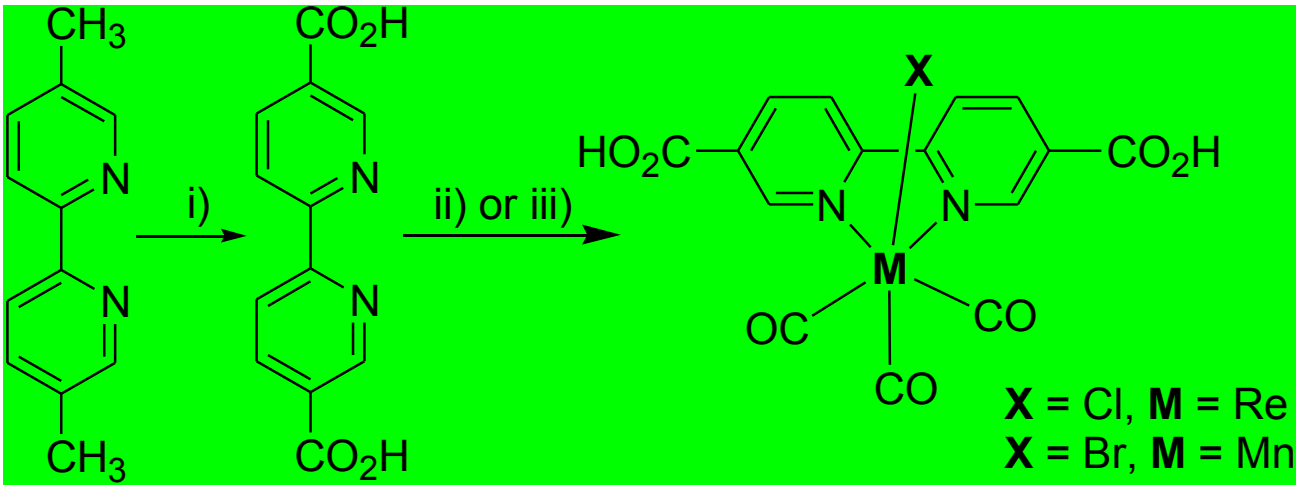


i) CH_3Cl, $AlCl_3$ (Caution: aluminum chloride reacts vigorously with water and releases HCl fumes. Dry conditions are required!); ii) fuming sulfuric acid (Caution: H_2SO_4 is highly corrosive!); iii) CH_2N_2 (Caution: diazomethane is highly toxic by inhalation or skin and eyes contact!); iv) Bu_4NOH, *p*-chloranil; v) H_2SO_4.

Figure S31 - Synthesis of tris(2,4,6-trichloro-3,5-dicarboxy)methyl radical according to Roques *et al.*[35]

1.32 - 2,2′-Bipyridine-5,5′-dicarboxylic acid

Complexes:
Bromido-[(2,2'-bipyridine)-5,5'-dicarboxylic acid-k-*N,N*']triscarbonylrhenium (I)
Chlorido-[(2,2'-bipyridine)-5,5'-dicarboxylic acid-k-*N,N*']triscarbonylmanganese (I)

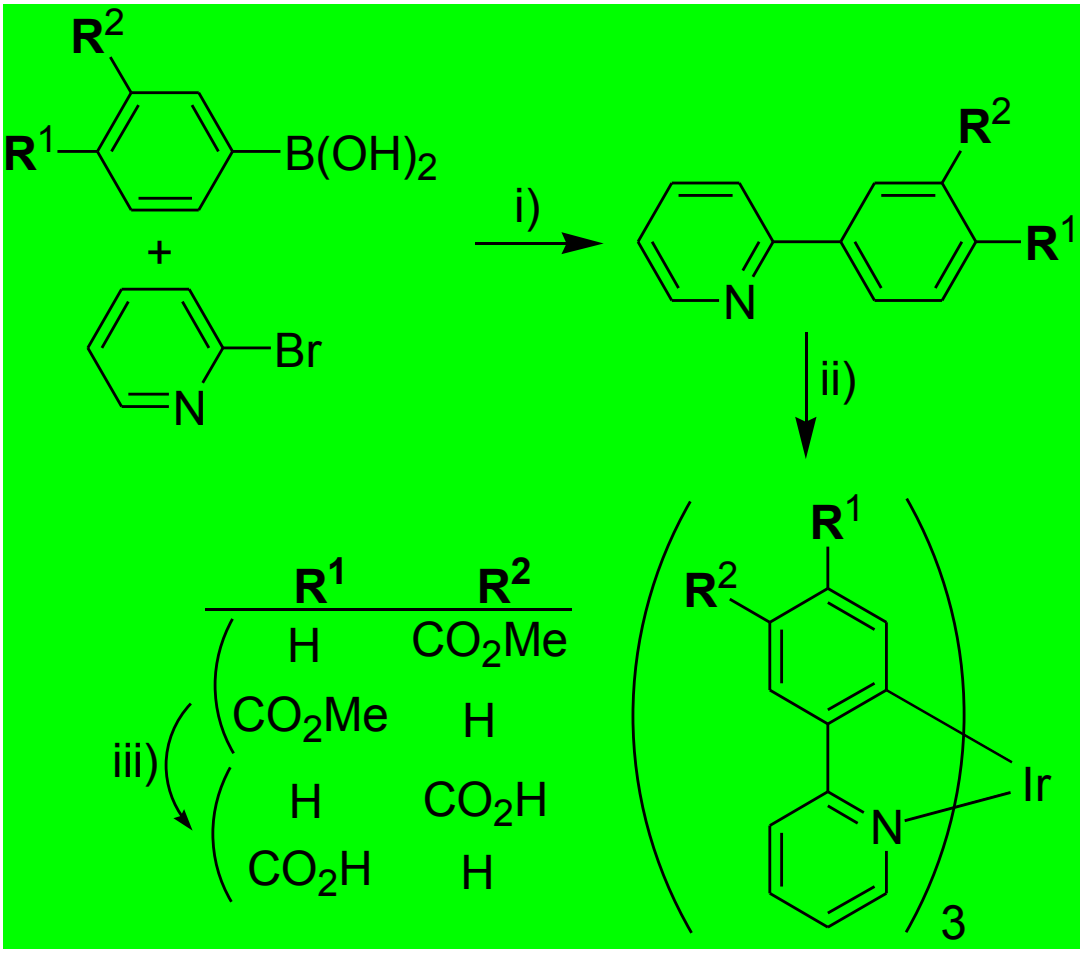


i) a) $KMnO_4$, H_2O, 70 ºC, 24 h; b) NaOH; c) HCl; ii) $Re(CO)_5Cl$, dry ethanol/toluene (1:1), 80 ºC, 2 d; iii) $Mn(CO)_5Br$, THF/toluene (1:1), N_2, 90 ºC, 2 h.

Figure S32 - Synthesis of 2,2′-bipyridine-5,5′-dicarboxylic acid [step i)], according to Nelissen *et al.*[36] and Venema *et al.*,[37] and of its complexes [step ii) or iii)] according to Blake *et al.*[38]

1.33 - 3-(Pyridin-2-yl)benzoic acid *and* 4-(Pyridin-2-yl)benzoic acid

Complexes:
tris(3-(Pyridin-2-yl)benzoic acid-k*N*,kC_2')iridium (III)
tris(4-(Pyridin-2-yl)benzoic acid-k*N*,kC_2')iridium (III)



i) THF, $NaHCO_3$, $Pd(dppf)Cl_2$, 70 ºC, 2 d; ii) Ethylene glycol, methyl 3-(2-pyridyl)benzoate, $IrCl_3 \cdot 3H_2O$, microwave irradiation (300 W, 120 ºC, 1 min); iii) a) THF/EtOH (1:1), NaOH, 70 ºC, overnight; b) HCl.

Figure S33 - Synthesis of 3-(pyridin-2-yl)benzoic acid and 4-(pyridin-2-yl)benzoic acid, and of their complexes with iridium (III) according to Xie *et al.*[39]

2 - References

1. X. Lin, A. J. Blake, C. Wilson, X. Z. Sun, N. R. Champness, M. W. George, P. Hubberstey, R. Mokaya and M. Schroder, *J. Am. Chem. Soc.*, 2006, **128**, 10745-10753.

2. A. G. Wong-Foy, O. Lebel and A. J. Matzger, *J. Am. Chem. Soc.*, 2007, **129**, 15740-15741.

3. M. Plabst and T. Bein, *Inorg. Chem.*, 2009, **48**, 4331-4341.

4. J. A. Groves, P. A. Wright and P. Lightfoot, *Inorg. Chem.*, 2005, **44**, 1736-1739.

5. J. P. S. Mowat, J. A. Groves, M. T. Wharmby, S. R. Miller, Y. Li, P. Lightfoot and P. A. Wright, *J. Solid State Chem.*, 2009, **182**, 2769-2778.

6. X. S. Wang, S. Q. Ma, K. Rauch, J. M. Simmons, D. Q. Yuan, X. P. Wang, T. Yildirim, W. C. Cole, J. J. Lopez, A. de Meijere and H. C. Zhou, *Chem. Mat.*, 2008, **20**, 3145-3152.

7. M. V. Vasylyev, E. J. Wachtel, R. Popovitz-Biro and R. Neumann, *Chem.-Eur. J.*, 2006, **12**, 3507-3514.

8. D. M. Connor, S. D. Allen, D. M. Collard, C. L. Liotta and D. A. Schiraldi, *J. Org. Chem.*, 1999, **64**, 6888-6890.

9. V. Lozan, P. Y. Solntsev, G. Leibeling, K. V. Domasevitch and B. Kersting, *Eur. J. Inorg. Chem.*, 2007, 3217-3226.

10. M. Dincă, A. Dailly, C. Tsay and J. R. Long, *Inorg. Chem.*, 2008, **47**, 11-13.

11. Z. P. Demko and K. B. Sharpless, *J. Org. Chem.*, 2001, **66**, 7945-7950.

12. A. Ritzen and T. Frejd, *Eur. J. Org. Chem.*, 2000, 3771-3782.

13. O. K. Farha, A. O. Yazaydin, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat. Chem.*, 2010, **2**, 944-948.

14. P. Pachfule, R. Das, P. Poddar and R. Banerjee, *Cryst. Growth Des.*, 2010, **10**, 2475-2478.

15. P. Lama, A. Aijaz, E. C. Sanudo and P. K. Bharadwaj, *Cryst. Growth Des.*, 2010, **10**, 283-290.

16. D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, 1962, **84**, 3370-3374.

17. J. P. Cornelissen, J. H. Vandiemen, L. R. Groeneveld, J. G. Haasnoot, A. L. Spek and J. Reedijk, *Inorg. Chem.*, 1992, **31**, 198-202.

18. S. Shimomura, M. Higuchi, R. Matsuda, K. Yoneda, Y. Hijikata, Y. Kubota, Y. Mita, J. Kim, M. Takata and S. Kitagawa, *Nat. Chem.*, 2010, **2**, 633-637.

19. Q. Yue, J. Yang, G. H. Li, G. D. Li and J. S. Chen, *Inorg. Chem.*, 2006, **45**, 4431-4439.

20. G. Z. Yuan, C. F. Zhu, W. M. Xuan and Y. Cui, *Chem.-Eur. J.*, 2009, **15**, 6428-6434.

21. S. Sivakumar, M. L. P. Reddy, A. H. Cowley and K. V. Vasudevan, *Dalton Trans.*, 2010, **39**, 776-786.

22. F. Einberg, *J. Org. Chem.*, 1970, **35**, 3978-3980.

23. Q. Y. Li, G. W. Yang, X. Y. Tang, Y. S. Ma, W. Yao, F. Zhou, J. Chen and H. Zhou, *Cryst. Growth Des.*, 2010, **10**, 165-170.

24. Z. R. Qu, Z. Xing, B. Z. Wu, X. Z. Li and G. F. Han, *Z. Anorg. Allg. Chem.*, 2009, **635**, 39-42.

25. P. H. Dinolfo, M. E. Williams, C. L. Stern and J. T. Hupp, *J. Am. Chem. Soc.*, 2004, **126**, 12989-13001.

26. S. Dapperheld, E. Steckhan, K. H. G. Brinkhaus and T. Esch, *Chem. Berichte*, 1991, **124**, 2557-2567.

27. K. C. Stylianou, R. Heck, S. Y. Chong, J. Bacsa, J. T. A. Jones, Y. Z. Khimyak, D. Bradshaw and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2010, **132**, 4119-4130.

28. J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982-986.

29. J. A. Musich and H. Rapoport, *J. Am. Chem. Soc.*, 1978, **100**, 4865-4872.

30. O. R. Evans, D. R. Manke and W. B. Lin, *Chem. Mat.*, 2002, **14**, 3866-3874.

31. O. R. Evans, H. L. Ngo and W. B. Lin, *J. Am. Chem. Soc.*, 2001, **123**, 10395-10396.

32. S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 2607-2614.

33. T. Tu, T. Maris and J. D. Wuest, *J. Org. Chem.*, 2008, **73**, 5255-5263.

34. D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nat. Mater.*, 2003, **2**, 190-195.

35. N. Roques, D. Maspoch, N. Domingo, D. Ruiz-Molina, K. Wurst, J. Tejada, C. Rovira and J. Veciana, *Chem. Commun.*, 2005, 4801-4803.

36. H. F. M. Nelissen, M. C. Feiters and R. J. M. Nolte, *J. Org. Chem.*, 2002, **67**, 5901-5906.

37. F. Venema, H. F. M. Nelissen, P. Berthault, N. Birlirakis, A. E. Rowan, M. C. Feiters and R. J. M. Nolte, *Chem.-Eur. J.*, 1998, **4**, 2237-2250.

38. A. J. Blake, N. R. Champness, T. L. Easun, D. R. Allan, H. Nowell, M. W. George, J. Jia and X. Z. Sun, *Nat. Chem.*, 2010, **2**, 688-694.

39. Z. G. Xie, L. Q. Ma, K. E. deKrafft, A. Jin and W. B. Lin, *J. Am. Chem. Soc.*, 2010, **132**, 922-923.